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## Quantum size effects and enhancement of the oscillator strength of excitons in chains of silicon atoms

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We have studied the size-dependent optical properties of confined excitons in chainlike Si-backbone polymers with 5–110 Si atoms. The blueshift of the lowest exciton state was observed with decreasing number of Si atoms. In chains having 20 Si atoms or less, the oscillator strength per Si atom for the lowest exciton linearly increases with increasing number of Si atoms. The radiative-decay rate of excitons is in proportion to the square of the number of Si atoms. These results are experimental evidence of the quantum size effect of excitons in chains of Si atoms.

Considerable interest has been focused on the study of low-dimensional semiconductor nanostructures because they exhibit a wealth of quantum phenomena and have a potential as future optoelectronic devices. Recently, many attempts have been made to produce a quasi-direct-gap semiconductor nanostructure made from indirect-gap semiconductors.<sup>1,2</sup> For example, additional photoluminescence lines have been reported in clusters and quantum wires of Si and Ge,<sup>3–5</sup> and clusters and wires of Si and Ge will eventually serve as optoelectronic materials. However, it is difficult to control the number of atoms in clusters and wires, and it is difficult to produce very small clusters and very thin wires. Therefore, optical properties in clusters and wires of Si and Ge are not well understood. In particular, there are few experimental studies of optical properties in small clusters<sup>6</sup> and we have little information on the quantum size effect in small semiconductor clusters. Optical studies of clusters and wires containing a few to several thousand atoms help to understand how molecules evolve into solids.<sup>7</sup>

Natural analogues of clusters and wires are oligomers and/or polymers. Modern organic synthesis and purification techniques allow us to produce materials with controlled molecular weight. These techniques have many advantages over other techniques<sup>3–5</sup> for the production of thin wires. In this paper, we report observation of size-dependent optical properties of confined excitons in chains of Si atoms synthesized by a chemical method.

The chainlike Si-backbone polymers, chains of Si atoms, with molecular structure,  $\text{EtO}-(\phi\text{-Si-CH}_3)_N\text{-OEt}$  were synthesized and purified by using the method described in Ref. 8. (Here “ $\phi$ ” and “Et” represent, respectively, phenyl and ethyl.) The molecular weight of polymers was checked by using a gel permeation chromatography. The average number of Si atoms in chains,  $N$ , was varied as follows:  $N = 5, 10, 20, 85$ , and  $110$ .

The absorption spectra of chainlike Si-backbone polymers solved in tetrahydrofuran (THF) were measured in order to eliminate electronic interactions between chains. The concentration of Si atoms in THF solution was  $1.67 \times 10^{-5}$  mol/dm<sup>3</sup>. On the other hand, for photo-

luminescence spectrum measurements, solid thin films were also prepared on a quartz substrate from THF solution. Photoluminescence spectra were measured by using a 325-nm excitation light from a He-Cd laser or a 313-nm excitation light from a Hg-Xe lamp. The calibration for the spectral sensitivity of the measuring system was performed by using a tungsten standard lamp. Picosecond temporal decay of luminescence under 1-ps and 305-nm laser excitation of  $\sim 1$  pJ per pulse was measured by using a monochromator of subtractive dispersion and a synchroscan streak camera. The temporal resolution of this system was about 30 ps. We checked that there is no significant difference in the luminescence spectrum and lifetime between solid films and solutions.

Figure 1 shows extinction coefficients per mole of Si atom ( $\epsilon_{\text{Si}}$ ) spectra and normalized photoluminescence spectra of chainlike Si polymers. A sharp absorption peak in a chain of Si atoms of  $N = 110$  indicates a quasi-one-dimensional electronic system and sharp absorption and emission peaks are due to the lowest one-dimensional (1D) exciton state delocalized in the Si backbone.<sup>9</sup> With a decrease in the number of Si atoms in chains, the absorption peak of the lowest exciton state is shifted to the higher energy (blueshift) and  $\epsilon_{\text{Si}}$  of the lowest exciton state<sup>10</sup> decreases.

Figure 2 shows the absorption peak of the lowest exciton state and the peak of photoluminescence as a function of the number of Si atoms in chains. The size effect of absorption and photoluminescence spectra are clearly observed in chains having 20 Si atoms or less. It is considered that the blueshift of the absorption peak is explained by a one-dimensional quantum well model. However, simple effective-mass models are not employed to explain the observed blueshift of the absorption spectrum in small semiconductor clusters.<sup>7</sup> The size dependence of the lowest excitation energy  $E_L$  of one-dimensional Si-backbone materials is approximately and phenomenologically given by<sup>11</sup>

$$E_L = E_{1D} + [q/(N/2 + p)]^2(E_2 - E_{1D}),$$

where  $p = 2/(\pi - 2)$  and  $q = \pi/(\pi - 2)$ .  $E_2$  and  $E_{1D}$  are the lowest excitation energies of disilane (6.2 eV) and the

quasi-one-dimensional Si-backbone polymer (3.66 eV), respectively. This equation gives interpolated  $E_L$  values between disilane ( $N=2$ ) and one-dimensional Si polymer with very large molecular weights ( $N \rightarrow \infty$ ). The calculated curve using the above equation is given by the solid line and roughly agrees with the experimental results. The blueshift of the absorption peak is due to the quantum confinement of the exciton on the Si skeleton.

Figure 3 shows the chain length dependence of the oscillator strength per Si atom for the lowest exciton  $f_1$ , calculated from the absorption spectra. The oscillator strength  $f_1$  is directly proportional to the integrated area of the absorption peak in diluted solutions as follows:

$$f_1 = 10^3 \ln(10) (mc / \pi h e^2 N_A) \int_{E_1}^{E_2} \epsilon_{Si} dE,$$

where  $m$  is the mass of electrons,  $c$  the velocity of light,  $e$  the charge of electrons,  $h$  the Planck constant,  $N_A$  the Avogadro number. Absorption areas of the lowest exciton,  $\int_{E_1}^{E_2} \epsilon_{Si} dE$  are those surrounded by the solid and dotted lines plotted in Fig. 1, where the high-energy tail of the lowest peak and the low-energy tail of the second peak are estimated by using Gaussian functions and the dotted lines are optimum tails of Gaussian profiles. Thus

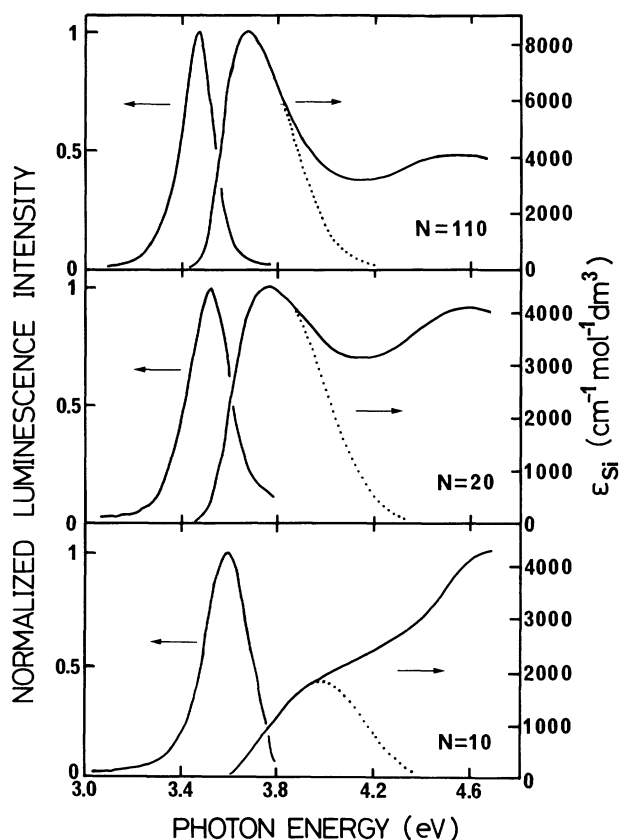


FIG. 1. Extinction coefficients per Si atom ( $\epsilon_{Si}$ ) spectra and normalized photoluminescence spectra in chainlike Si polymers.  $N$  is the average number of Si atoms in chains. Absorption areas of the lowest excitons are those surrounded by solid lines and dotted lines.

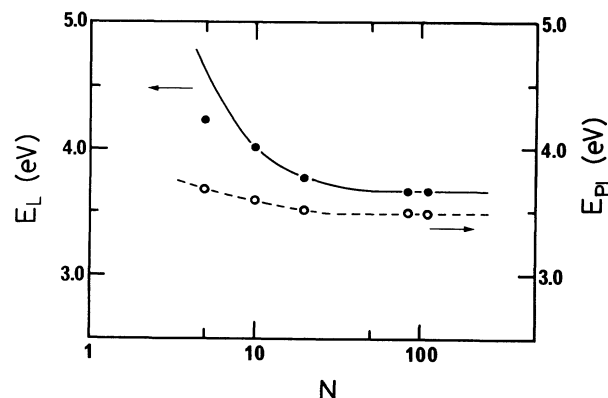


FIG. 2. The absorption peak energy of the lowest exciton state  $E_L$  and the peak energy of photoluminescence spectra  $E_{PL}$  as a function of the number of Si atoms in chains,  $N$ . Solid and open circles correspond to the peak energies of absorption and photoluminescence, respectively. The solid line is calculated by a simple quantum well model discussed in the text. The broken line is a guide to the eye.

we can estimate the oscillator strength of the lowest exciton  $f_1$ . The oscillator strength per Si atom,  $f_1$ , is linearly proportional to the number of Si atoms and then saturates to a constant value; in Si chains of  $N \leq 20$ ,  $f_1$  is approximately given by  $f_1 \propto N$ . If chains of Si atoms are solids in nature, the oscillator strength per atom is almost independent of the number of atoms.<sup>12</sup> Therefore, we believe that the size-dependent region is the continuous transition of Si chains from molecular to solid forms and long chains become solidlike in optical properties. To our limited knowledge, there is no theoretical work of the size dependence of the oscillator strength of excitons in small "molecularlike" clusters and chains.

Figure 4 shows picosecond temporal changes in the exciton luminescence at the peak energies. The lumines-

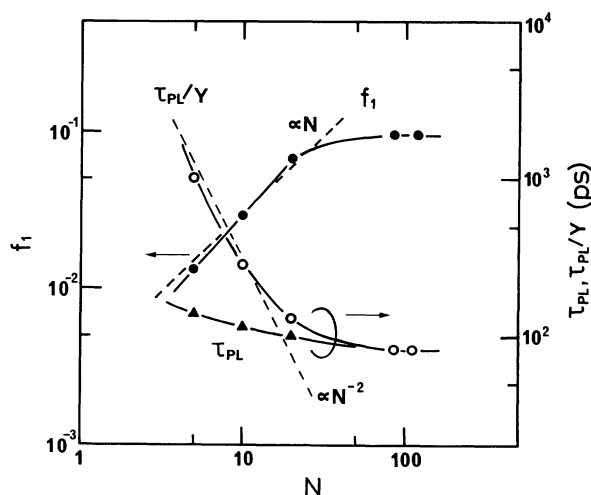


FIG. 3. The oscillator strength of confined excitons  $f_1$ , the lifetime of photoluminescence at the peak energy  $\tau_{PL}$ , and  $\tau_{PL}/Y$  as a function of Si atoms in chains,  $N$ .  $Y$  is the relative quantum yield of photoluminescence.

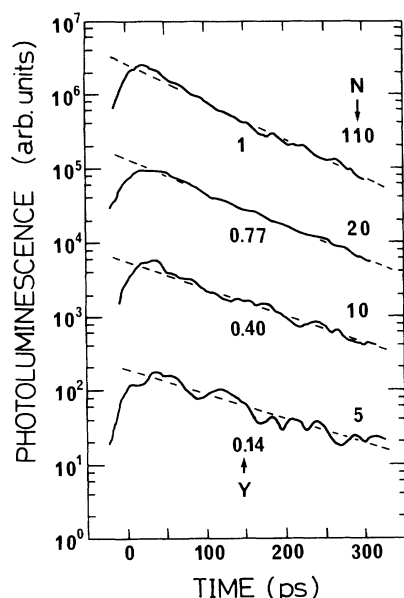


FIG. 4. Picosecond temporal changes in luminescence due to the exciton at peak energies. The luminescence decay is fitted by a single exponential.  $Y$  is the relative quantum yield of photoluminescence.

cence decay was approximately described as a single exponential having time constant  $\tau_{PL}$  and  $\tau_{PL}$  increases with decreasing  $N$ . A single exponential decay of luminescence implies that the luminescence is determined by a simple relaxation process. Here, we assume that the lifetime of luminescence  $\tau_{PL}$  is determined by two relaxation channels having the radiative decay rate  $\tau_R^{-1}$  and the non-radiative decay rate  $\tau_{NR}^{-1}$ . Since the quantum yield of luminescence  $\eta$  is given by  $\tau_R^{-1}/(\tau_R^{-1} + \tau_{NR}^{-1})$ , the radiative decay rate  $\tau_R^{-1}$  is given by  $\eta/\tau_{PL}$ . Although the absolute values of  $\eta$  in Si polymers were not obtained experimentally, we can use here the relative yield  $Y$  for  $\eta$  in order to discuss the size dependence of the radiative decay rate of the exciton and make  $Y=1$  for a chain of  $N=110$ . The values of  $Y$  for each Si polymer chain are shown in Fig. 4. The lifetime of photoluminescence  $\tau_{PL}$  and the radiative decay time  $\tau_{PL}/Y$  are plotted in Fig. 3. The radiative decay time  $\tau_{PL}/Y$  increases with the decrease of Si atoms,  $N$ . In particular, in chains of  $N \leq 20$ ,  $\tau_{PL}/Y$  is approximately given by  $\tau_{PL}/Y \propto N^{-2}$ . The radiative decay time depends on the oscillator strength per chain. If the exciton is a coherent excitation over the Si chain, the radi-

ative decay time is inversely proportional to  $Nf_1$ . Since  $f_1 \propto N$  in chains of  $N \leq 20$ , the radiative decay time is in proportion to  $N^{-2}$ . The size dependence of radiative decay time  $\tau_{PL}/Y$  confirms that of the oscillator strength  $f_1$  of the lowest exciton. These size dependences imply that in chains having 20 Si atoms or less, the exciton is coherently excited over the chain of Si atoms.

The above considerations and conclusions are supported by the following discussion. Hochstrasser and co-workers<sup>13</sup> reported that the quantum yield of photoluminescence in a polymethylphenylsilane with very large molecular weight is about 0.1 and the lifetime of luminescence is 73 ps. In our work, the lifetime of photoluminescence is about 76 ps in a Si chain having  $N=110$ . Using  $\eta=0.1$  and  $\tau_{PL}=76$  ps, we can estimate the radiative decay rate of excitons delocalized on the Si backbone,  $\tau_R^{-1}$ . On the other hand, the oscillator strength per Si atom,  $f_1$ , directly gives the radiative decay rate based on one Si atom,  $\tau_{abs}^{-1}$ . The ratio  $\tau_{abs}/\tau_R$  in a Si chain of  $N=110$  is about 24, which means that the excitons are delocalized over about 24 Si atoms. Therefore, we conclude that in chains having Si atoms smaller than about 24, the excitons are confined in chains of Si atoms and the size dependence of optical properties of excitons can be observed. In fact, our experiments show that the blueshift of the exciton state energy and the size dependence of the oscillator strength are clearly and experimentally observed in short chains having 20 Si atoms or less. The exciton is coherently excited over about 20 Si atoms on the Si-backbone chain and the exciton has the oscillator strength depending on the number of Si atoms in chains. Our results are experimental evidence of size-dependent optical properties of excitons in chains of Si atoms.<sup>14</sup>

In conclusion, we observed the quantum size effect of the oscillator strength of confined excitons in chainlike Si-backbone polymers. The oscillator strength per Si atom for the lowest excitons is linearly proportional to the number of Si atoms in chains having 20 Si atoms or less and saturates to a value in long chains. This study gives experimental evidence of the continuous transition of a Si chain from molecular to solid form.

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- <sup>14</sup>In chainlike Si-backbone polymers ( $\sigma$ -electron conjugated systems), a sharp photoluminescence is observed with essentially no Stokes shift: photoluminescence is due to free-exciton recombination. On the other hand, in  $\pi$ -electron conjugated carbon-backbone polymers, a very large Stokes shift is usually observed: photoluminescence may be caused by the localized exciton recombination. Therefore, in this work, the significant size dependence of optical properties of confined excitons was observed in chains of Si atoms.